On the Mechanism of the Absorption Spectra of Solutions.

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On the theory of electrons the colour of bodies is explained in three ways: (1) The body is homogeneous and the electrons in it execute vibrations about their mean positions in the molecules. (2) The body is homogeneous and the electrons in it are free to move about from molecule to molecule as is the case with metals. (3) The body may consist of small spheres or grains of colouring matter embedded in a homogeneous transparent medium. We get an absorption spectrum with bands in it from (1) and (3), but not from (2). We can distinguish (3) from (1) by the polarised light scattered by the grains; the quantity of light scattered is, however, small in comparison with the quantity absorbed in the grains. The granular structure is also revealed by ultramicroscopic examination. This investigation is concerned only with (1).

An absorption band, then, corresponds to a principal oscillation of the molecule or whatever system the absorption spectrum is characteristic of. Let the principal co-ordinates of this system be q_1, $q_2, \ldots q_n$. Then, when a light wave is being transmitted across the medium, if the motion is not damped, the typical equation of motion assumes the form

$$a_r\ddot{q}_r + c_r q_r = Q', \tag{1}$$

Q′ being the resultant electric intensity at the point. Q′ is related to Q, the electric intensity of the light wave, by the relation

$$Q' = Q + gP, \tag{2}$$

P being the polarisation and g a constant. To take account of absorption introduce the dissipation function,

$$2F = b_{11}\dot{q}_1^2 + b_{22}\dot{q}_2^2 + \ldots + 2b_{12}\dot{q}_1\dot{q}_2 + \ldots.$$

The typical equation thus becomes

$$a_r\ddot{q}_r + b_{r1}\dot{q}_1 + b_{r2}\dot{q}_2 + \ldots + b_{rr}\dot{q}_r \ldots + b_{rn}\dot{q}_n + c_r q_r = Q'. \tag{3}$$

Let the transmitted radiation be of the type $e^{i\theta t}$. If, as is usual, we assume that the friction terms do not appreciably affect the periods, we may solve the other $(n-1)$ equations on the assumption that the motion is undamped and substitute the results above. We obtain

$$q_1(c_1 - a_1\theta^2) = Q' \ldots q_n(c_n - a_n\theta^2) = Q',$$

and on substituting

$$(c_r + b_{rr} i\theta - a_r\theta^2)\, q_r + \frac{b_{r1} Q' i\theta}{c_1 - a_1\theta^2} \dots + \frac{b_{rn} Q' i\theta}{c_n - a_n\theta^2} = Q'.$$

Thus
$$q_r = \frac{Q'\left[1 - i\theta\left(\frac{b_{r1}}{c_1 - a_1\theta^2} \dots + \frac{b_{rn}}{c_n - a_n\theta^2}\right)\right]}{c_r - a_r\theta^2 + b_{rr} i\theta}. \qquad (4)$$

Let K be the specific inductive capacity of the medium. Then

$$K = 1 + 4\pi P/Q. \qquad (5)$$

The polarisation must be a linear function of the co-ordinates, therefore

$$P = f_1 q_1 + f_2 q_2 \dots + f_n q_n. \qquad (6)$$

Using (2), (5), and (6) and writing $(\nu - i\kappa)^2$ for K, we obtain

$$\frac{(\nu - i\kappa)^2 - 1}{(\nu - i\kappa)^2 \frac{g}{4\pi} + \left(1 - \frac{g}{4\pi}\right)} = 4\pi\Sigma\frac{f_r q_r}{Q'}. \qquad (7)$$

We shall now assume that we are dealing with a well-defined absorption band, one on each side of which there is a more or less transparent region. We shall also assume that we are dealing with solutions and coloured glasses which transmit an appreciable amount of light, when a millimetre or two thick, even at the darkest point of the visible spectrum. We can then neglect κ^2 in comparison with ν^2 and can also neglect the variation in ν produced by the absorption band. As the index of refraction of the solvents and glasses varies only 1 or 2 per cent. throughout the visible spectrum, ν may be considered constant throughout the absorption band.

The imaginary part of the left side of (7) is

$$-2\nu\kappa \Big/ \left\{\nu^2 \frac{g}{4\pi} + \left(1 - \frac{g}{4\pi}\right)\right\}^2.$$

If q_r refer to the band under consideration, the only term on the right side of (7) which has an appreciable imaginary part is q_r/Q'. Rewriting (4),

$$\frac{q_r}{Q'} = \frac{1 - iA}{(c_r - a_r\theta^2) + i b_{rr}\theta} = \frac{(c_r - a_r\theta^2) - A b_{rr}\theta - i b_{rr}\theta - iA(c_r - a_r\theta^2)}{(c_r - a_r\theta^2)^2 + b_{rr}{}^2\theta^2},$$

where A is a function of θ. Hence

$$2\nu\kappa = \frac{C(b_{rr}\theta + A\{c_r - a_r\theta^2\})}{(c_r - a_r\theta^2)^2 + b_{rr}{}^2\theta^2}, \qquad (8)$$

where C is a constant given by

$$4\pi f_r \left\{\frac{\nu^2 g}{4\pi} + \left(1 - \frac{g}{4\pi}\right)\right\}^2.$$

So far the discussion has been as general as possible. Assume, now, that the band is due to a class of electrons vibrating about their mean positions; assume, also, as Drude has it in his Optics, that this class of electrons is uninfluenced by any others in the field. Then $A = 0$ and $C = 4\pi Ne$, where N is the number of electrons of this class per unit volume. Let m be the mass of one of them and e its charge in electrostratic units. Then $a_r = m/e$.

We may thus rewrite (8) in the simpler form

$$\kappa = 2\pi Neb_{rr}\theta \Big/ \nu \left\{ \left(c_r - \frac{m}{e}\theta^2\right)^2 + b_{rr}^2\theta^2 \right\}. \tag{9}$$

An expression of this type has been used to represent absorption bands by Ketteler, Pflüger, the author, and others, the constants being chosen to fit the experimental results, and it has been found that the only term in it varying appreciably with θ is the bracket in the denominator. We may therefore rewrite (9)

$$\kappa = 2\pi Neb_{rr}\theta_0 \Big/ \nu \left\{ \left(c_r - \frac{m}{e}\theta^2\right)^2 + b_{rr}^2\theta_0^2 \right\}, \tag{10}$$

where θ_0 is the value of θ at the maximum, θ_0 being given by $\theta_0^2 = c_r e/m$.

The maximum value of κ, $\bar{\kappa}$, is given by $\bar{\kappa} = 2\pi Ne/(\nu b_{rr}\theta_0)$. Let θ_1 be the value of θ for which κ has half its maximum value; then

$$\left(c_r - \frac{m}{e}\theta_1^2\right) = \pm b_{rr}\theta_0.$$

Substituting for c_r,

$$\frac{m}{e}(\theta_0^2 - \theta^2) = \pm b_{rr}\theta_0.$$

Hence
$$\bar{\kappa} = \frac{2\pi Ne^2}{\nu m(\theta_0^2 - \theta_1^2)}.$$

Let us now substitute for θ_0 and θ_1, $2\pi v/\lambda_0$ and $2\pi v/\lambda_1$, where v is the velocity and λ_0, λ_1 the wave-length of light *in vacuo*. Then

$$\bar{\kappa} = \frac{Ne^2\lambda_0^2\lambda_1^2}{2\pi\nu m v^2(\lambda_1^2 - \lambda_0^2)}.$$

Express e in electromagnetic units and v^2 will disappear from the denominator. Also, since λ_1 does not differ much from λ_0, we may write

$$\frac{\lambda_0^2\lambda_1^2}{\lambda_1^2 - \lambda_0^2} = \frac{\lambda_0^3}{2(\lambda_1 - \lambda_0)}.$$

Hence
$$\bar{\kappa} = \frac{Ne^2\lambda_0^3}{4\pi\nu m(\lambda_1 - \lambda_0)}. \tag{11}$$

Let p be the number of electrons per molecule of colouring matter belonging to the absorption band under consideration. Then N/p is the number of molecules per unit volume. Let c be the concentration of the solution in gramme-molecules per litre and let $m_{\rm H}$ be the mass of an atom of hydrogen. Then $c/(1000\, m_{\rm H})$ is also equal to the number of molecules of dissolved colouring matter per unit volume. Therefore

$$\frac{\rm N}{p} = \frac{c}{1000\, m_{\rm H}}.$$

Substituting for N from (11), we obtain

$$\frac{pe}{m} = 4000\,\pi \frac{\nu\kappa}{c} \frac{m_{\rm H}}{e} \frac{(\lambda_1 - \lambda_0)}{\lambda_0^3}. \qquad (12)$$

If we substitute 9660 for $e/m_{\rm H}$, this gives

$$\frac{pe}{m} = 1{\cdot}300 \frac{\nu\kappa}{c} \frac{(\lambda_1 - \lambda_0)}{\lambda_0^3}. \qquad (13)$$

Formula (13) holds only on the very special assumptions made by Drude. Absorption bands in general have not the simple shape demanded by Drude's theory. I have, nevertheless, applied the formula to all the well-defined absorption bands on which I could get measurements. In view of our ignorance of the subject, any method that may throw light on the mechanism of absorption deserves to be followed up.

There is a great diversity of ways for specifying the absorption of a solution, but this does not make much difference in applying the formula. If the tables give the fraction of the incident light transmitted by a power of 10 or e, λ_1 is the wave-length for which the index has half its maximum value. On the other hand, if the fraction of the incident light transmitted is given directly, and I be its maximum value, λ_1 is the wave-length for which the fraction transmitted is $\sqrt{\rm I}$. In most cases we get a somewhat different result according as we take λ_1 on the red or violet side of the band; I have, as a rule, taken it on the red side, as that is generally better defined. Once λ_1 was chosen it was never altered, no matter what value of pe/m it gave. The following table (p. 610) gives some results.

The measurements of Katz and Kalandek agree as well as can be expected in the case of eosin in water, but differ in the case of fuchsin in alcohol. We cannot, however, be certain that the substance used was the same in each case. Some of Katz's results were not utilised as they promised nothing new. Zsigmondy's results are given in the form of curves and the numbers were taken from the curves. The colouring matter exists in these glasses as an oxide or silicate, and apparently Garnett's theory does not apply.* Pulfrich does not state the strength of solution employed, and I had to standardise his results by making a rough determination of the index of extinction for one wave-length. There are no measurements available on the didymium salts, but *pe/m* for their bands would probably have a low value, owing to their narrowness and the strength of the solution necessary to make them visible. It is not possible to utilise the work that has been done on the ultra-violet absorption of organic substances as it is not quantitative.

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* Prof. Zsigmondy informs me that he has not examined them ultramicroscopically, but that it is to be assumed that they are optically homogeneous.

Substance.	λ_0.	λ_1.	*pe/m*.	Source of data.
Fuchsin in alcohol	550	585	1·8 10^7	Stanislaw Kalandek, 'Phys. Zeit.,' 9 Jahrg., pp. 128—135.
,, aniline	565	595	1·7 10^7	
Phloxin in water	515	560	1·4 10^7	
Crystal violet in alcohol	575	611	4·9 10^7	
,, aniline	605	635	4·7 10^7	
Corallin in alcohol	465	515	1·6 10^6	
,, aniline	455	505	1·7 10^6	
Methylene blue in water	665	690	5·4 10^6	
,, aniline	675	660	7·7 10^6	
Water blue in water	575	646	8·1 10^6	
Eosin in water	515	533	6·9 10^6	
Eosin in water	516	525	9·2 10^6	Georg. J. Katz, 'Inaug.-diss. Erlangen,' 1898.
,, alcohol	527	542	2·3 10^7	
,, turpentine	539	550	6·5 10^5	
Cyanine in alcohol	587	609	5·8 10^6	
,, ether	597	628	6·9 10^4	
,, chloroform	597	615	7·8 10^6	
,, benzol	608	627	1·5 10^4	
Hexamethylpararosaniline in water	587	597	3·4 10^6	
,, ,, alcohol	608	624	1·3 10^7	
,, ,, chloroform	618	630	2·4 10^6	
Fuchsin in water	550	578	1·7 10^6	
,, chloroform	550	570	2·4 10^6	
,, alcohol	558	578	1·6 10^6	
Pentamethylmonophenylpararosaniline in chloroform	582	605	4·3 10^7	
Pentamethylmonophenylpararosaniline in water	592	606	3·6 10^6	
Pentamethylmonophenylpararosaniline in alcohol	582	608	1·7 10^7	
Pentamethylmonophenylpararosaniline in ether	582	598	1·0 10^5	
Pentamethylmonophenylpararosaniline in benzol	603	620	8·4 10^5	
Cobalt chloride in water	504	540	2·5 10^3	Houstoun and Russell, 'Roy. Soc. Edin. Proc.,' vol. 29, Part II, p. 68.
Uranyl nitrate in water	486	491	34	
	473	478	75 ?	
Three glasses coloured with CoO	644	668	5·0 10^4	R. Zsigmondy, 'Ann. d. Phys.,' (4), vol. 4, 1901, p. 60.
	631	660	3·0 10^4	
	640	700	3·0 10^4	
Two glasses coloured with Cr_2O_3	620	690	3·2 10^4	
	655	725	1·2 10^4	
Three glasses coloured with NiO	640	670	1·3 10^4	
	640	672	1·0 10^4	
	610	662	1·1 10^4	
Potassium permanganate in water	547	570	5·1 10^5	C. Pulfrich, 'Wied. Ann.,' vol. 14, 1881, p. 177.

The values of pe/m obtained for the anilin colouring matters, when dissolved in water, alcohol, or chloroform, are very striking, since the ratio of the charge to the mass of an electron is about $1{\cdot}8 \times 10^7$. *We are evidently dealing here with electrons, and Drude's assumptions are not far wrong.* When the solvent is benzol or ether, the values of pe/m are considerably lower. This raises the question whether the colouring matter is not in colloid solution in these cases. We have no observations to go upon, but in this connection a paper by Dr. Sheppard* is interesting. It may be noticed that a calculation made by Drude from the dispersion of solid cyanine gave $pe/m = 8{\cdot}5 \times 10^6$ for its absorption band.

The values of pe/m obtained for the inorganic salts suggest ions, though here potassium permanganate is difficult to place. Probably, though, we shall have to fall back on the more general theory and possibly also take account of the scattering of light by granules.

In conclusion, I should like to acknowledge my indebtedness to Prof. Larmor for the benefit of his criticism.

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* S. E. Sheppard, "On the Influence of their State in Solution on the Absorption Spectra of Dissolved Dyes," 'Roy. Soc. Proc.,' May, 1909.